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Glossary

Absolute configuration (Section 7.3): The actual three-dimensional arrangement of groups around a chirality center.

Acetal (Section 18.9): The product of the addition of two equivalents of an alcohol to an aldehyde or a ketone; $R_2C(OR')_2$.

Acetylide anion (Section 10.8): A carbon nucleophile generated by treating 1-alkynes with a very strong base, such as sodium amide; $RC{\equiv}C{:}^-$.

Achiral molecule (Section 7.1): A molecule that is superimposable on its mirror image.

Acidity constant (K_a) (Section 4.2): An equilibrium constant for the reaction of an acid with water as a base; used as a measure of the strength of an acid. For a general acid, HA, the equation for K_a is

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Activation energy (Section 4.3): The energy required to surmount the energy barrier separating reactants and products.

Acyl group (Section 12.5): A carbonyl group with an attached alkyl group.

Addition polymer or **chain-growth polymer** (Section 24.1): A polymer formed by a chain mechanism, where one initiator molecule causes a large number of monomers to react to form one polymer molecule.

Addition reaction (Chapter 10): A reaction that results in the addition of two groups to opposite ends of a multiple bond.

Alkaloid (Section 28.7): A nitrogen-containing natural product that occurs primarily in higher plants and in some fungi, such as mushrooms.

Alkyl group (Section 2.7): The part of a compound that has carbons that are only singly bonded to other carbons and hydrogens.

Alkylation reaction (Section 20.3): A reaction that results in the attachment of an alkyl group to the reactant.

Allowed reaction (Section 22.2): A pericyclic reaction that is energetically favorable because the electrons in the occupied MOs do not increase in energy.

Allyl group (Section 5.5): The $CH_2{=}CHCH_2{-}$ group.

Alpha-carbon (α-carbon) (Section 12.3): The carbon adjacent to a functional group; most commonly used to refer to the carbon adjacent to a carbonyl group.

Amorphous solid (Section 24.5): A solid in which the individual molecules have a random arrangement; a glassy solid with no order in the arrangement of its molecules.

Amphoteric compound (Section 26.2): A compound that can act as either an acid or a base.

Angle strain (Section 6.4): Destabilization, usually found in compounds having three- or four-membered rings, that occurs when the orbitals of a bond do not point directly at each other, so the amount of overlap is decreased.

Annulene (Section 16.10): A name sometimes given to rings that contain alternating single and double bonds in a single Lewis structure.

Anomers (Section 25.3): Diastereomers that are formed by cyclization of a carbohydrate with differing configurations at the new stereocenter.

Anti addition (Section 10.2): The addition of groups to opposite faces of a double bond.

Anti conformation (Section 6.3): Conformation in which the dihedral angle between two groups on adjacent atoms is 180°.

Anti elimination (Section 9.3): Elimination of groups from a conformation in which the dihedral angle between them is 180°. This is the preferred geometry in the E2 reaction.

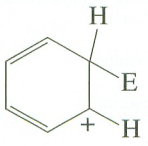
Antiaromatic compound (Section 16.5): A compound that is destabilized because of the presence of conjugated cycle of p orbitals containing $4n$ electrons.

Antibonding MO (Section 3.2): A MO that is higher in energy than the AOs that combine to form it.

Anti-periplanar bonds (Section 9.3): Bonds with a dihedral angle of 180°.

Aprotic solvent (Section 8.11): A solvent that does not have a hydrogen bonded to nitrogen or oxygen and therefore cannot hydrogen bond.

Arenium ion (Section 17.1): The carbocation formed by addition of an electrophile to a benzene derivative.



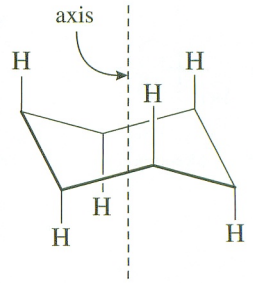
Arenium ion

Aromatic compound (Sections 16.1 and 16.5): A compound that is especially stable because of the presence of conjugated cycle of p orbitals containing $4n + 2$ electrons.

Atactic polymer (Section 24.2): A polymer with random configurations at its many stereocenters.

Atomic orbital (Section 3.1): The region about the nucleus of an atom where, if the orbital contains an electron, the probability of finding that electron is very high.

Axial bond (Section 6.5): In the chair conformation of cyclohexane, a bond that is parallel to the axis of the ring.



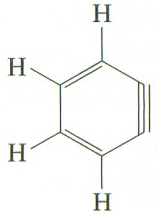
Axial CH bonds

Axial strain energy (Section 6.7): The amount of destabilization caused by a group in the axial position in the chair conformation of cyclohexane.

Base ion (Section 15.4): The most abundant ion in the mass spectrum.

Benzyl group (Section 12.1): The $PhCH_2{-}$ group.

Benzyne (Section 17.12): A highly reactive intermediate that has a benzene ring with a formal triple bond.



Benzyne

Boat conformation (Section 6.5): The boat-shaped conformation of cyclohexane that has no angle strain but does have some steric strain and some torsional strain.

Boat conformation

Bond disconnections (Section 23.5): The imaginary process of breaking bonds at or near the functional groups in a compound during the process of retrosynthetic analysis.

Bond dissociation energy (Section 2.2): The amount of energy that must be added in the gas phase to break the bond in a homolytic manner.

Bonding MO (Section 3.2): A MO that is lower in energy than the AOs that combine to form it.

Bromonium ion (Section 11.4): A three-membered ring containing a positively charged bromine atom; an intermediate formed in the addition of bromine to an alkene.

Bronsted-Lowry acid (Section 4.1): A proton donor.

Bronsted-Lowry base (Section 4.1): A proton acceptor.

Cahn-Ingold-Prelog sequence rules (Section 6.2): Rules that are used to assign priorities to groups attached to a stereocenter so that the configuration of the compound can be designated.

Carbanion (Section 2.1): A carbon with three bonds, an unshared pair of electrons, and a negative charge.

Carbene (Section 11.8): A reactive species having a carbon with only two bonds and an unshared pair of electrons.

Carbenoid (Section 11.8): An organometallic species that reacts like carbene.

Carbocation (Sections 2.1 and 8.6): A carbon with three bonds and a positive charge.

Carbohydrate (Section 25.1): Naturally occurring compounds, often with the general formula $C_x(H_2O)_x$, that are polyhydroxy aldehydes or ketones and derivatives formed from these; includes sugars and starches.

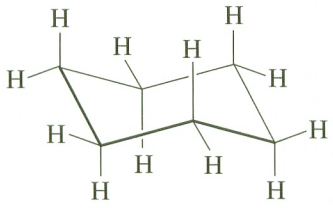
Carbonyl group (Section 12.3): A CO double bond.

Carboxy group (Section 12.4): A carbonyl group with an attached hydroxy group.

Chain reaction (Section 21.6): A reaction in which a reactive intermediate, such as a radical, reacts with a normal molecule, ultimately generating a molecule of product and regenerating the original reactive intermediate, which then causes another reaction cycle to occur. A chain reaction involves three types of steps: initiation, propagation, and termination.

Chain-growth polymer. See *Addition polymer.*

Chair conformation (Section 6.5): The chair-shaped conformation of cyclohexane that has no angle strain and has no torsional strain either because it is perfectly staggered about all the CC bonds. It is strain free.



Chair conformation

Chemical shift (Sections 14.1 and 14.3): The position of an absorption on the *x*-axis in an NMR spectrum; provides information about the local environment of the atom that is responsible for the absorption.

Chirality center (Section 7.2): A carbon or other tetrahedral atom bonded to four different groups; a type of stereocenter.

Chiral molecule (Section 7.1): A molecule that is not superimposable on its mirror image.

Chromophore (Section 15.2): The part of a molecule that is responsible for the absorption of ultraviolet or visible light.

Cis–trans isomers (Section 6.1): Stereoisomers that differ in the placement of groups on one side or the other of a double bond.

Codon (Section 27.3): A series of three bases in a nucleic acid polymer that specifies a particular amino acid.

Concerted reaction (Section 8.3): A reaction that occurs in one step.

Condensation polymer or step growth polymer (Section 24.8): A polymer formed from monomers with two reactive functional groups by normal reactions, such as ester formation, between the functional groups.

Configuration (Section 6.2): The three-dimensional arrangement of groups about a stereocenter in a molecule.

Conformation (Section 6.3): A shape that a molecule can assume by rotation about a single bond.

Conformational analysis (Section 6.3): Analysis of the energies of the various conformations of a compound.

Conjugate acid (Section 4.1): The acid formed by protonation of a base in an acid–base reaction.

Conjugate addition or **1,4-addition** (Section 18.10): The addition of a nucleophile to the β-carbon of an α,β-unsaturated carbonyl compound.

Conjugate base (Section 4.1): The base formed by the loss of a proton from an acid in an acid–base reaction.

Conjugated molecule (Section 3.6): A molecule that has a series of three or more overlapping parallel *p* orbitals on adjacent atoms.

Connectivity (Section 1.7): The arrangement of bonded atoms in a structure.

Conrotation (Section 22.1): Rotation of orbitals in the same direction in an electrocyclic reaction.

Constitutional isomers (Section 1.7): Compounds that have the same molecular formula but a different arrangement (connectivity) of bonded atoms.

Coupling constant (J_{ax}) (Section 14.4): The separation between two adjacent peaks in a group of peaks that results from coupling in an NMR spectrum.

Covalent bonding (Section 1.4): Bonding that results from atoms sharing electrons in order to arrive at the same number of electrons as a noble gas.

Cross-link (Section 24.7): A group that connects separate polymer chains by covalent bonds.

Crystalline solid (Section 24.5): A solid in which the individual molecules are arranged with a very high degree of order.

Cycloaddition reaction (Section 22.5): A pericyclic reaction in which two molecules react to form two new sigma bonds between the end atoms of their pi systems, resulting in the formation of a ring.

Degenerate orbitals (Section 3.1): Orbitals with the same energy.

Degree of unsaturation (DU) (Section 2.4): The total number of multiple bonds plus rings in a compound. The DU is calculated by subtracting the actual number of hydrogens in a compound from the maximum number of hydrogens and dividing the result by 2.

Delocalized MO (Sections 3.2 and 3.6): A MO that extends around more than two atoms.

DEPT-NMR (distortionless enhancement by polarization transfer) (Section 14.9): A technique used in ^{13}C-NMR that allows the number of hydrogens attached to each carbon to be determined.

Dextrorotatory, (*d*) or **(+)** (Section 7.4): Clockwise rotation of plane-polarized light.

Diastereomers (Section 7.5): Non–mirror-image stereoisomers.

1,3-Diaxial interaction (Section 6.7): An interaction that destabilizes two axial groups on the same face of a cyclohexane ring because of steric crowding between them.

Dienophile (Section 22.6): The species, most often an alkene or alkyne, that acts as the two-electron component in a Diels-Alder reaction.

Dihedral angle (Section 6.3): The angle between a marker group on the front atom and one on the back atom in the Newman projection.

Dipolar ion or **zwitterion** (Section 26.2): A neutral compound containing a covalently linked cation and anion.

Dipole moment (μ) (Section 1.9): The product of the amount of charge separation in a molecule times the distance of the charge separation.

Disaccharide (Section 25.6): A carbohydrate formed from two monosaccharide units that are connected by a glycosidic bond.

Disrotation (Section 22.1): Rotation of orbitals in opposite directions in an electrocyclic reaction.

Downfield (Section 14.3): A chemical shift at a higher delta value in the NMR spectrum.

E (Section 6.2): Letter used to designate the isomer of an alkene that has the high priority groups on opposite sides of the double bond.

E1 reaction or **unimolecular elimination reaction** (Section 9.5): An elimination reaction that occurs in two steps through a carbocation intermediate.

E2 reaction or **bimolecular elimination reaction** (Section 9.2): An elimination reaction that follows a concerted mechanism in which a base removes a proton simultaneously with the departure of the leaving group.

Eclipsed conformation (Section 6.3): Conformation in which the bonds on one atom are directly in line with the bonds on the adjacent atom when a Newman projection is viewed.

Eclipsed conformation

Electrocyclic reaction (Section 22.3): A pericyclic reaction that forms a sigma bond between the end atoms of a series of conjugated pi bonds within a molecule.

Electromagnetic spectrum (Section 13.3): The range of electromagnetic radiation (light), from very energetic cosmic rays to low-energy radio waves.

Electronegativity (Section 1.9): Electron-attracting ability of an atom.

Electronic transition (Section 15.1): The excitation of an electron from an occupied MO to an antibonding MO.

Electrophile (Section 8.1): An electron-poor species that seeks an electron-rich site; similar to a Lewis acid.

Electrophilic addition reaction (Section 11.1): A reaction that results in the addition of two groups, an electrophile and a nucleophile, to the carbons of a CC double or triple bond.

Electrophilic aromatic substitution reaction (Section 17.1): A reaction in which an electrophile is substituted for a hydrogen on an aromatic ring.

Elimination reaction (Section 8.14, Chapter 9): A reaction in which groups (most commonly a proton and a leaving group) are lost from adjacent atoms, resulting in the formation of a double bond.

1,1-Elimination (Section 11.8): An elimination of two groups from the same carbon to produce a carbene; also called an α-elimination.

1,2-Elimination (Section 9.1): An elimination of two groups from adjacent atoms to produce a pi bond; also called a β-elimination.

Enantiomers (Section 7.1): Nonsuperimposable mirror-image stereoisomers.

Endergonic reaction (Section 8.3): A reaction for which $\Delta G°$ is positive; the products are higher in energy than the reactants and the reaction favors the reactants at equilibrium.

Endothermic reaction (Section 8.3): A reaction for which the enthalpy change ($\Delta H°$) is positive.

Enol (Section 11.6): A compound with a hydroxy group attached to a CC double bond.

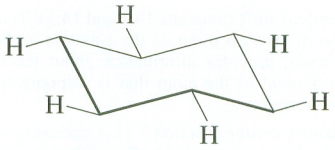
Enolate ion (Chapter 20): A carbanion adjacent to a carbonyl group.

Enthalpy change (ΔH) (Section 2.6): The heat of reaction; $\Delta H > 0$ for an endothermic reaction and $\Delta H < 0$ for an exothermic reaction.

Entropy change (ΔS) (Section 2.6): Entropy is a measure of disorder. Processes that increase the disorder in a system ($\Delta S > 0$) are favored.

Epoxide (oxirane) (Section 10.10): A three-membered cyclic ether.

Equatorial bond (Section 6.5): In the chair conformation of cyclohexane, a bond that projects outward from the "equator" of the ring.



Equatorial CH bonds

Equilibrium arrows (Section 1.8): Two arrows that are used to represent an equilibrium reaction where the reactants and products are interconverting. $\rightleftharpoons$

Excited state (Section 3.1): Any state that is higher in energy than the ground state.

Exergonic reaction (Section 8.3): A reaction for which $\Delta G°$ is negative; the products are lower in energy than the reactants and the reaction favors the products at equilibrium.

Exothermic reaction (Section 8.3): A reaction for which the enthalpy change ($\Delta H°$) is negative.

Fat (Section 28.8): A triester formed from glycerol and long, linear-chain carboxylic acids, known as fatty acids.

Fingerprint region (Section 13.9): The region below 1500 cm^{-1} in the infrared spectrum that contains numerous absorptions due to single bond stretches and a variety of bending vibrations. Because of the large number of bands, this is the region where comparison of the spectrum of an unknown to that of a known compound can establish the identity of the unknown.

Fischer projection (Section 7.8): A two-dimensional drawing of a chiral molecule in which the chirality center is represented as a cross with the atom at its center. Although the four bonds to the chirality center are shown in the plane of the page, the horizontal bonds project above the plane of the page and the vertical bonds project behind the page.

Forbidden reaction (Section 22.2): A pericyclic reaction that is energetically unfavorable because the electrons in the occupied MOs increase in energy.

Formal charge (Section 1.7): The approximate charge that is present on an atom in a covalent structure. It is the number of valence electrons in the neutral atom before any bonding (this is the same as the group number of the atom), minus the number of unshared electrons on the atom in the structure of interest, and also minus one-half the number of shared electrons on that atom.

Free energy of activation, $\Delta G^{\ddagger}$ (Sections 4.4 and 8.3): The energy difference between the transition state and the reactants.

Free energy change ($\Delta G°$) (Section 4.2): The difference in energy between the products and reactants. It is related to the enthalpy change, the entropy change, and the equilibrium constant for a reaction by the equations $\Delta G° = \Delta H° - T\Delta S° = -RT \ln K$. For a reaction to be spontaneous, K must be greater than 1 and $\Delta G°$ must be negative.

Frequency (ν) (Section 13.1): The number of wave cycles that pass a point in a second.

Frontier orbitals (Section 22.2): The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Functional group (Section 2.7): The group of atoms and bonds that determines the chemical behavior of a compound.

Furanose (Section 25.3): A cyclic form of a carbohydrate that has a five-membered ring.

Gauche conformation (Section 6.3): Conformation in which the dihedral angle between two groups on adjacent atoms is 60°.

Geminal hydrogens (Section 14.4): Hydrogens bonded to the same carbon.

Glycoside (Section 25.4): An acetal formed by the reaction of a carbohydrate hemiacetal with an alcohol in the presence of acid.

Grignard reagent (organomagnesium halide) (Section 18.5): An organometallic species with a carbon–magnesium bond; RMgX.

Ground state (Section 3.1): The lowest energy state.

Halogens (Section 1.5): The elements of group 7A of the periodic table: F, Cl, Br, and I.

Hammond postulate (Section 8.6): The structure of the transition state for a reaction step is more similar to that of the species (reactant or product of that step) to which it is closer in energy.

Heteroatom (Section 12.5): An atom other than C and H.

Heterolytic bond cleavage (Section 21.1): A bond-breaking process in which both electrons of that bond remain with one of the atoms; ions are produced.

Highest occupied MO (HOMO) (Sections 15.1 and 22.2): The highest-energy orbital that is occupied by electrons.

Hofmann's rule (Section 9.4): The major product of an elimination reaction has fewer alkyl groups bonded to the carbons of the double bond (the less highly substituted product). The Hofmann elimination follows this rule.

Homolytic bond cleavage (Section 21.1): A bond-breaking process in which one electron of the bond remains with each of the atoms; radicals are produced.

Hückel's rule (Section 16.5): A cyclic, fully conjugated, planar molecule with $4n + 2$ pi electrons (n = any integer) is aromatic.

Hund's rule (Section 3.1): Electrons first occupy degenerate orbitals singly, with the same (parallel) spins until they all contain one electron.

Hydride ion (Sections 8.14 and 10.7): A hydrogen with a pair of electrons and a negative charge; $H:^-$.

Hydrocarbon (Sections 2.3 and 5.1): A compound made up of only carbon and hydrogen.

Hydrogen bond (Section 2.5): A relatively strong attraction of a hydrogen bonded to an electronegative atom (O, N, or F) to another electronegative atom (O, N, or F).

Hydrogenolysis (Section 23.1): A reaction in which a single bond is broken by hydrogen and a catalyst.

Hydrolysis reaction (Section 10.2): A reaction in which water is both the nucleophile and solvent.

Hydrophilic compound (Section 2.6): A compound that has a favorable interaction with water because of its polar nature.

Hydrophobic compound (Section 2.6): A compound that has an unfavorable interaction with water because of its nonpolar nature.

Hyperconjugation (Section 8.7): A stabilizing interaction of a sigma bonding MO with an empty *p* orbital on an adjacent atom.

Inductive effect (Section 4.5): The effect of a dipole in a molecule on a reaction elsewhere in that molecule.

Infrared (IR) spectroscopy (Section 13.4): A type of spectroscopy that employs infrared light. IR spectroscopy uses transitions between vibrational energy levels to provide information about the functional groups that are present in a compound.

Integral (Section 14.1): The area under a group of peaks in a ^{1}H-NMR spectrum; proportional to the number of hydrogens that produce that group of peaks.

Intermolecular reaction (Section 8.13): A reaction that involves two separate molecules.

Intramolecular reaction (Section 8.13): A reaction in which both reacting groups are part of the same molecule.

Inversion of configuration (Section 8.4): The stereochemical result of a reaction in which the product has the opposite relative configuration to the reactant.

Ionic bonding (Section 1.3): Bonding that results when atoms gain or lose electrons to form ions with the same number of electrons as one of the noble gases.

Isoelectric point (pI) (Section 26.2): The pH at which an amino acid has an overall charge of zero.

Isotactic polymer (Section 24.4): A polymer with identical configuration at all its stereocenters.

Leaving group (Section 8.1): The group that is replaced in a substitution reaction.

Levorotatory, (*l*) or (−) (Section 7.4): Counterclockwise rotation of plane-polarized light.

Lewis acid (Section 4.1): An electron pair acceptor.

Lewis base (Section 4.1): An electron pair donor.

Lewis structures (Section 1.5): Structures that show all the electrons in the valence shells of the atoms as dots.

London force (Section 2.5): The attraction between nonpolar molecules that results from the interaction of an instantaneous dipole with an induced dipole.

Lowest unoccupied MO (LUMO) (Sections 15.1 and 22.2): The lowest-energy empty MO.

Macromolecule (Section 24.1): A very large molecule. This term is often applied to polymer molecules, which are composed of a very large number of monomers (hundreds or even thousands) and therefore are extremely large.

Markovnikov's rule (Section 11.2): In addition reactions of HX to alkenes, the H bonds to the carbon with more hydrogens (fewer alkyl substituents) and the X bonds to the carbon with fewer hydrogens (more alkyl substituents). A more modern version of Markovnikov's rule, based on mechanistic reasoning, is that the electrophile adds so as to form the more stable carbocation.

Mass spectrometry (Section 15.4): An instrumental technique used to measure the molecular mass of a compound; provides information about the structure of the compound from the masses of fragments that are produced from the compound.

***meso*-Stereoisomer** (Section 7.5): A compound that contains chirality centers but is not chiral because it has the same chirality centers, but with opposite configurations, placed symmetrically in the compound, so it has an internal plane of symmetry.

Methylene (Section 11.8): The simplest carbene (carbon with only two bonds and an unshared pair of electrons); CH_2.

Methylene group (Section 5.3): The CH_2 group.

Molecular ion ($M^+_\bullet$) (Section 15.4): A radical cation produced in a mass spectrometer that has the same mass as the original molecule but has one less electron.

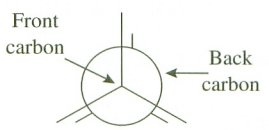
Molecular orbital (MO) (Section 3.2): An electron orbital that extends around more than one atom.

Monomer (Section 24.1): One of the individual units that are bonded together to form a polymer.

Monosaccharide (Section 25.1): A carbohydrate formed from one sugar unit.

Multiplicity (Sections 14.1 and 14.4): The number of peaks in each absorption in a ^{1}H-NMR spectrum; provides information about the other hydrogens that are near the hydrogen(s) that produces the peaks.

Newman projection (Section 6.3): An end-on view of a bond so that one atom of the bond is directly behind the other. By convention, the front atom is represented by the intersection of its bonds and the back atom is represented by a circle.



Newman projection

Node (Section 3.1): A region of an orbital where the value of the wave function equals zero, and therefore the electron density is zero.

Nonbonding AO (Section 3.3): An atomic orbital that is not involved in bonding.

Nonpolar bond (Section 1.9): A bond between atoms of similar electronegativities in which the electrons are shared nearly equally.

Nuclear magnetic resonance (NMR) spectroscopy (Section 14.1): A type of spectroscopy that uses transitions between the energy states of certain nuclei when they are in a magnetic field to supply information about the hydrocarbon part of a compound. There are two NMR techniques that are of most use to organic chemists: proton magnetic resonance (^{1}H-NMR) spectroscopy, which provides information about the hydrogens in a compound, and carbon-13 magnetic resonance spectroscopy (^{13}C-NMR), which provides information about the carbons in a compound.

Nucleophile (Section 8.1): An electron-rich species that seeks an electron-poor site; similar to a Lewis base.

Nucleoside (Section 27.1): A component of a nucleic acid containing a sugar, either ribose or 2′-deoxyribose, and a base, a cyclic nitrogen-containing compound.

Nucleotide (Section 27.1): A nucleoside that has a phosphate group attached to the sugar.

Octet rule (Section 1.5): Atoms of the second period of the periodic table need eight electrons in their outer shell to be most stable.

Optically active (Section 7.4): A compound that rotates the plane of polarization of plane-polarized light.

Organometallic compound (Section 18.5): A compound with a covalent carbon–metal bond. Because the metal is less electronegative than carbon, the bond is polarized in the opposite direction to that found in most organic compounds; that is, the negative end of the dipole is on the carbon and the positive end is on the metal. These often make useful carbon nucleophiles.

Oxidation reaction (Section 10.14): A reaction that results in an increase in oxygen content of the compound and/or a decrease in hydrogen content.

Pauli exclusion principle (Section 3.1): No two electrons can have all four quantum numbers the same.

Peptide (Section 26.5): A term used for a polymer of amino acids that is smaller than a protein.

Percarboxylic acid (Section 11.9): A carboxylic acid that has an extra oxygen and an oxygen–oxygen bond; RCO_3H.

Pericyclic reaction (Section 22.1): A concerted reaction that proceeds through a cyclic transition state in which two or more bonds are made and/or broken.

Phenyl group (Section 12.1): A benzene ring group; Ph—.

Pheromone (Section 23.5): A compound used by animals, especially insects, for communication.

Photolysis reaction (Section 22.1): A reaction caused by light.

Pi (π) bond (Section 3.4): A bond formed by overlap of parallel *p* orbitals.

Plane of symmetry (Section 7.2): An imaginary plane that passes through the center of an object so that one-half of the object is the mirror image of the other half; also called a mirror plane.

Plane-polarized light (Section 7.4): A light beam in which the electromagnetic field of all the waves oscillate in a single plane.

Polar bond (Section 1.9): A bond with charge separation because the atoms involved have different electronegativities.

Polarimeter (Section 7.4): An instrument used to determine the amount by which a compound rotates the plane of polarization of plane-polarized light.

Polymer (Chapter 24): A very large molecule made up of repeating units.

Polysaccharide (Section 25.7): A polymeric carbohydrate formed from monosaccharides that are linked by glycosidic bonds.

Primary carbon (Section 5.3): A carbon that is bonded to one other carbon.

Primary natural products (Chapter 28): Naturally occurring compounds that are found in all types of organisms and are the products of primary metabolism; includes carbohydrates, amino acids, proteins, and nucleic acids.

Product development control (Section 9.4): More of the lower-energy product being formed in a reaction because the stability of the products results in a somewhat more stable transition state.

Prostaglandins (Section 28.9): A group of naturally occurring carboxylic acids that are related to the fatty acids and have been found to be involved in a number of important physiological functions, including the inflammatory response, the production of pain and fever, the regulation of blood pressure, the induction of blood clotting, and the induction of labor.

Protecting group (Sections 18.9 and 23.1): A group that is used to protect one functional group in a complex compound from reacting while a reaction is occurring at another functional group in the molecule.

Protein (Section 26.5): A term usually reserved for a naturally occurring polymer that contains a relatively large number of amino acid units and has a molecular mass in the range of a few thousand or larger.

Protic solvent (Section 8.11): A solvent that has a hydrogen bonded to nitrogen or oxygen. Water, alcohols, and carboxylic acids are examples of protic solvents.

Pyranose (Section 25.3): A cyclic form of a carbohydrate that has a six-membered ring.

Quaternary carbon (Section 5.3): A carbon that is bonded to four carbons.

***R* configuration** (Section 7.3): Term used to designate the configuration of a carbon chirality center. When viewed so that the bond from the chirality center to the group with the lowest priority is pointed directly away from the viewer, the direction of the cycle of the remaining groups, proceeding in decreasing order of priority, is clockwise.

Racemic mixture (Section 7.4): An equal mixture of enantiomers. Also called a racemate.

Racemization (Section 8.4): The stereochemical result of a reaction in which complete randomization of stereochemistry has occurred in the product (50% inversion and 50% retention).

Radical (Section 2.1 and Chapter 21): A species with an odd number of electrons.

Radical anion (Section 21.10): A species that has both an odd number of electrons and a negative charge.

Radical cation (Section 15.4): A species with both an odd number of electrons and a positive charge.

Rate-limiting step or **rate-determining step** (Section 8.6): The step in a mechanism that has the highest energy transition state and therefore determines the rate of the reaction.

Reaction mechanism (Sections 4.3 and 8.2): The individual steps in a reaction that show how the nuclei and the electrons move, how the bonds change as the reaction proceeds, and the order in which the bonds are made and broken.

Reactive intermediate (Section 8.6): A high-energy, reactive species, such as a carbocation, that is formed along a reaction pathway. Under most conditions it has a very short lifetime.

Reduction reaction (Section 10.14): A reaction that results in a decrease in oxygen content of the compound and/or an increase in hydrogen content.

Regiochemistry (Section 9.4): The result of a reaction that can produce two or more structural isomers.

Regioselective reaction (Section 11.2): A reaction that produces predominantly one possible orientation (regiochemistry) in a reaction but does form some of the product with the other orientation.

Regiospecific reaction (Section 11.2): A reaction that produces only one of two possible orientations (regiochemistries) in a reaction.

Relative configuration (Section 7.3): The configuration of a chiral center relative to that of a chiral center in another molecule.

Resolution (Section 7.7): The process of separating the enantiomers of a racemic mixture.

Resonance arrow (Sections 1.8 and 3.6): The double-headed arrow ($\longleftrightarrow$) used to show that structures are resonance structures.

Resonance hybrid (Section 1.8): The actual structure of a compound that is represented by two or more resonance structures. It is a blend of the extremes represented by the various resonance structures.

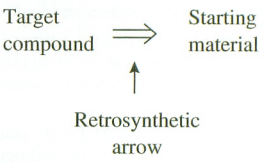
Resonance stabilization energy (Sections 1.8 and 3.7): The extra stabilization of a compound because of resonance.

Resonance structures (Section 3.7): Structures for a compound that differ only in the position of multiple bonds and unshared electrons.

Retention of configuration (Section 8.4): The stereochemical result of a reaction in which the product has the same relative configuration as the reactant.

Retrosynthetic analysis (Section 10.15): The process of designing a synthesis by working backward from the target compound.

Retrosynthetic arrow (Section 11.14): An arrow used in the development of a synthetic scheme that points from the target to the reactant from which it can be prepared.



Ring-flip (Section 6.5): The conversion of one chair conformation of cyclohexane to another in a process that changes all axial bonds to equatorial and vice versa.

***S* configuration** (Section 7.3): Term used to designate the configuration of a carbon chirality center. When viewed so that the bond from the chirality center to the group with the lowest priority is pointed directly away from the viewer, the direction of the cycle of the remaining groups, proceeding in decreasing order of priority, is counterclockwise.

Saponification (Section 19.5): The hydrolysis of an ester under basic conditions.

Saturated compound (Section 5.5): A compound that does not contain multiple bonds.

Secondary carbon (Section 5.3): A carbon that is bonded to two carbons.

Secondary natural products (Chapter 28): Natural products that are usually produced from primary natural product precursors, such as amino acids or acetate ion, and, in general, are less widespread in occurrence than primary natural products.

Sigma (σ) bond (Section 3.2): A bond formed by overlap of orbitals that point directly toward each other so that its MO is symmetric about the internuclear axis.

Sigmatropic rearrangement (Section 22.8): The intramolecular migration of a group along a conjugated pi system.

S_N1 reaction or **unimolecular nucleophilic substitution reaction** (Section 8.6): A reaction in which the nucleophile replaces the leaving group at an sp^3-hybridized carbon in a two-step mechanism that proceeds through a carbocation intermediate.

S_N2 reaction or **bimolecular nucleophilic substitution reaction** (Section 8.3): A reaction in which the nucleophile replaces the leaving group at an sp^3-hybridized carbon in a one-step mechanism.

Solid phase synthesis (Section 26.7): A synthetic method in which a compound is attached to the surface of insoluble polymer beads. After a reaction is run on the compound, it is only necessary to collect the beads by filtration and wash them to remove any remaining reagent and isolate the product. Not only is the isolation procedure fast and simple but mechanical losses are minimized. After a number of reactions are run, the final product is cleaved from the polymer and isolated.

Solvolysis reaction (Section 9.7): A reaction in which the solvent acts as both the nucleophile and the solvent.

***sp*-Hybridized AOs** (Section 3.5): The two AOs formed from combining one *s* orbital and one *p* orbital. These AOs are used to form sigma bonds by atoms with linear geometry.

sp^2-Hybridized AOs (Section 3.4): The three AOs that are formed from combining one *s* orbital and two *p* orbitals. These AOs are used to form sigma bonds by atoms with trigonal planar geometry.

sp^3-Hybridized AOs (Section 3.3): The four AOs that are formed from combining one *s* orbital and three *p* orbitals. These AOs are used to form sigma bonds by atoms with tetrahedral geometry.

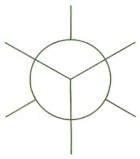
Specific rotation ([α]) (Section 7.4): The magnitude of rotation of plane-polarized light by a chiral compound at a concentration of 1 g/mL and a path length of 1 dm.

Spectroscopy (Chapter 13): The study of the interaction of electromagnetic radiation (light) with molecules.

Spectrum (Section 13.2): A plot of the amount of light that is absorbed versus the frequency or wavelength of the light.

Spin coupling (Section 14.5): The interaction of the small magnetic fields of nearby nuclei in an NMR experiment that results in the splitting of the absorption into multiple peaks.

Staggered conformation (Section 6.3): Conformation in which the bonds on one atom bisect the angle between the bonds on the adjacent atom when a Newman projection is viewed.



Staggered conformation

Step growth polymer. See *Condensation polymer.*

Stereocenter or **stereogenic atom** (Section 6.1): An atom at which the interchange of two groups produces a stereoisomer.

Stereochemistry (Chapter 6): The three-dimensional structure of a molecule.

Stereoelectronic requirement (Section 4.3): The orientation required for the orbitals of the reactants in order for the reaction to occur.

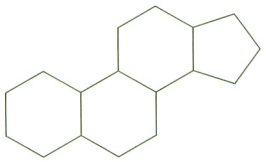
Stereoisomers (Chapter 6): Isomers that have the same bonds or connectivity but a different three-dimensional orientation of these bonds.

Stereoselective reaction (Section 11.4): A reaction that produces predominantly one stereoisomer in a reaction but does form some of the other stereoisomer.

Stereospecific reaction (Section 11.4): A reaction that produces only one of two possible stereoisomers in a reaction.

Steric strain (Section 6.1): Strain caused by repulsion between nonbonded atoms that results in distortion of bond lengths and/or bond angles.

Steroid (Section 28.5): A naturally occurring compound that has a tetracyclic ring system consisting of three fused six-membered rings and one five-membered ring.



Steroid ring system

Strain (Section 6.1): Any factor that destabilizes a molecule by forcing it to deviate from its optimum bonding geometry.

Structural isomers: See *Constitutional isomers.*

Substitution reaction (Chapter 8): A reaction in which one group bonded to carbon is replaced by another.

Syn addition (Section 11.7): The addition of groups to the same face of a double bond.

Syn-periplanar bonds (Section 9.3): Bonds with a dihedral angle of 0°.

Synthetic equivalent (Section 10.2): A species that is used in place of another reagent in a synthesis. A synthetic equivalent gives the same final product, usually in better yield, as the other reagent, although more steps are required.

Synthons (Section 23.5): Electrophilic and nucleophilic fragments generated by bond disconnections during retrosynthetic analysis.

Tautomers (Section 11.6): Structural isomers that differ only in the position of a hydrogen and a pi bond.

Terpene (Section 28.1): A compound that occurs naturally in plants and can be considered as resulting from the combination of isoprene units.

Tertiary carbon (Section 5.3): A carbon that is bonded to three carbons.

Tetrahedral intermediate (Section 18.1): The intermediate formed in a substitution reaction at a carbonyl carbon, in which a nucleophile bonds to the carbonyl carbon, resulting in the formation of an sp^3-hybridized carbon in the intermediate.

Thermolysis (pyrolysis) reaction (Section 22.1): A reaction caused by heat.

Thermoplastic polymer (Section 24.5): A polymer that is hard at room temperature but softens and eventually melts as it is heated.

Thermoset polymer (Section 24.9): A polymer that does not soften or melt on heating but becomes larger, harder, and more insoluble because cross-linking becomes more extensive.

Torsional strain (Section 6.3): Destabilization resulting from eclipsed bonds.

Transannular strain (Section 6.6): A type of strain that occurs in larger rings because of steric crowding of atoms on the opposite sides of the ring. Also called cross-ring strain.

Trans-diaxial elimination (Section 9.3): Elimination of axial groups on adjacent atoms on a cyclohexane ring. This is the preferred geometry for the E2 reaction with cyclohexane derivatives.

Transition state (Section 8.3): The structure of the complex at the maximum on the energy versus reaction progress curve and in which all the requirements for a reaction have been met.

Ultraviolet-visible (UV) spectroscopy (Section 15.1): A type of spectroscopy that employs ultraviolet or visible light; UV-visible spectroscopy uses transitions between electronic energy levels to provide information about the conjugated part of a compound.

Umpolung (polarity reversal) (Section 20.9): The formal reversal of the normal polarity of a functional group in synthetic reactions.

Unsaturated compound (Section 5.5): A compound that contains multiple bonds.

Upfield (Section 14.3): A chemical shift at a lower delta value in the NMR spectrum.

Valence bond theory (Section 3.2): A bonding model that uses overlap of AOs on the two bonded atoms to form MOs that are localized around these two atoms.

Valence electrons (Section 1.2): The electrons in the outermost electron shell.

Valence shell electron pair repulsion theory (VSEPR) (Section 1.10): A theory that is used to predict geometry based on the principle that pairs of electrons in the valence shell of an atom repel each other and try to stay as far apart as possible.

van der Waals forces (Section 2.5): The attraction between molecules that results from dipole–dipole interactions, dipole-induced dipole interactions, and instantaneous dipole-induced dipole (London force) interactions.

Vicinal hydrogens (Section 14.4): Hydrogens bonded to adjacent atoms.

Vinyl group (Section 5.5): The $CH_2{=}CH{-}$ group.

Vinyl polymer (Section 24.1): An addition polymer that is prepared from a monomer that contains a vinyl group.

Wavelength (λ) (Section 13.1): The distance of one complete cycle of the light wave; the distance between successive crests or troughs of the wave.

Wavenumber (Section 13.4): The reciprocal of wavelength (units are cm^{-1}); used in infrared spectroscopy.

Ylide (Section 18.7): A carbanion that is bonded to a positive phosphorus group.

Z (Section 6.2): Letter used to designate the isomer of an alkene that has the high priority groups on the same side of the double bond.

Zaitsev's rule (Section 9.4): The major product of an elimination reaction is the alkene with more alkyl groups on the carbons of the double bond (the more highly substituted product). Most E1 and E2 reactions follow this rule.

Zwitterion: See *Dipolar ion.*

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